Surface Characteristics of Unburned Carbon on Fly Ash and their Influence on Foam Index Testing

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The “Foam Index” test is the standard commercial screening test for quickly assessing the suitability of a particular fly ash as a concrete additive. The test is not standardized, and different organizations perform it in different ways. It may be performed with any of a number of commercial air entraining admixtures (AEAs) under a variety of conditions. We have studied some general factors which influence Foam Index (FI) values, and compared results of such testing with other characterizations of numerous fly ash samples from various utilities across the country.

In our work, we have compared the FI values given by two different AEAs which are in common usage. One is Darex-II™ from Grace Construction Products and the other is Air 40™ provided by Boral Material Technologies, Inc. These agents have been tested on a variety of samples thought to be representative of a variety of actual operating practices. A very wide range of LOI contents was represented, and both class C and class F ashes were examined. Our implementation of the FI test involved water dilution of the as-received AEA to a 10% (vol.) solution. The actual test involved placing 8 grams of Portland cement, 2 grams of the fly ash to be tested, and 25 ml of deionized water into a 70 ml jar which could be vigorously agitated following addition of an aliquot of AEA. A micropipette gun was used to add the diluted AEA solution dropwise, with a minimum droplet size of 0.01 ml, and uncertainties in results were typically ± 0.02 ml. The endpoint was judged to have been reached when after agitation for 15 seconds, bubbles remained on the surface of the water for more than 45 seconds. The FI value is simply the number of milliliters of AEA solution added to achieve the endpoint, less the FI value of a blank containing no fly ash. It is important to note that the rate of addition of drops influenced the observed endpoint in some cases. Quick addition of a large amount of AEA would lead to an apparent endpoint at a lower value FI than when the drops were added slowly. This is thought to be due to finite rate diffusion of the AEA into the pores of the unburned carbon, which is the sink for the AEA [1-4].

The results of the testing with the two different commercial products showed that there was in all cases a relatively constant multiplicative factor which related the FI for one AEA to that for the other. Thus while one AEA may be more “potent” than another, there did not appear to be any preferential adsorption of either AEA on one type of ash as opposed to another. Naturally, the extent of water dilution of the agent will determine the absolute value of FI. It was also observed that AEAs would tend to “age”. Over a period of several months, it was not uncommon for FI values to increase significantly. Thus absolute values of FI are generally not significant because they are influenced by dilution and aging. It is the relative behavior of different ash samples with a single AEA of constant properties that is important.

Earlier results indicated that unburned carbon surface plays an important role in determining the suitability of the ashes for concrete, at least as indicated by the FI test [1-4]. This is thought to be related to the role of carbon surface as the preferred site for adsorption of AEA from the mix. Adsorption of AEA destroys its ability to act as a bubble-forming surfactant in the mix. Carbon in fly ash presents a significant source of adsorptive surface in the typical mix, and it is not surprising that the suitability of ashes, relative to air entrainment in the concrete, appears to decrease with increasing carbon content in the ash. The carbon in fly ash may be viewed as being similar in behavior to activated carbons used for purification of water. Correlation of FI with carbon surface area in the ash is, however, only partially successful. This is because carbon surfaces may exist in both oxidized (polar) and unoxidized (non-polar) forms. It proved necessary to characterize the carbon surface for polarity to distinguish some otherwise very similar surfaces [3]. It is hypothesized that it is the non-polar surface which is active for adsorption of the AEA. Surface polarity of the remaining carbon may be influenced to a considerable extent by the combustion conditions that the ash has seen. These results suggest why factors influencing combustion can strongly influence the differing properties of similar LOI ashes.

The differences between class C and class F ashes could not, however, be fully explained even on the basis of surface area and polarity. Class C fly ashes typically exhibit rather low LOI values, but may still perform poorly in concrete. This can be because the carbon in class C ashes typically exhibits a higher surface area than the carbon in class F ashes. Still, there is a high degree of variability within the class C ashes, and many which have high surface area still do not give high FI values. Surface polarity could not explain the difference. The explanation of the difference between the good and bad ashes has to do with the nature of the porosity in the carbon. In order for the AEA to be adsorbed onto a carbon, it is not only necessary that there be adsorption sites provided by high surface area, but that there also be accessibility to these sites provided by sufficient number of large pores in the carbon. The numerous very small micropores in some class C ashes cannot be accessed by the AEA because of the absence of larger mesopores through which the AEA can quickly diffuse. This is a well-known problem in design of activated carbons for water purification; it is important in design of an effective carbon to have sufficient mesoporosity as well as microporosity.

Thus the behavior of different fly ashes in the FI test, and towards AEAs in general, is influenced by several factors. The first, and most important, is the amount of carbon in the ash. Keeping all other factors constant, the more carbon, the greater the potential for AEA adsorption and poor air entrainment. Beyond the amount of carbon, its total surface area, its content of mesoporosity, and its surface polarity can all play important roles in determining the AEA adsorption capacity of an ash. These characteristics are in large part pre-determined by the choice of coal feed to the boiler. The coals which lead to class C ashes will generally give carbons which are quite different in porosity than the coals which give class F ashes. The characteristics of the carbon surface, particularly polarity, can however, be influenced by the nature of the combustion process. This may be why in some low-NOx retrofits, despite the fact that there was no fuel switching and no dramatic increase in LOI, there may have been a significant degradation in ash quality.

References

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